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SYNTHESIS AND MICROSTRUCTURE OF HIGHLY ORIENTED $PbTiO_3$ THIN FILMS PREPARED BY A SOL-GEL METHOD

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ABSTRACT

Thin films of $PbTiO_3$ were deposited on fused silica, resistor-grade alumina, and single crystal (100) MgO by a sol-gel processing method. While the films deposited on silica and alumina substrates were randomly oriented and polycrystalline, highly {100} oriented $PbTiO_3$ films were grown on the MgO single crystals. The perovskite-type structure was observed with films deposited on the single crystal MgO and annealed at temperatures as low as 470°C, while a pyrochlore-type structure was observed with films on fused silica and alumina processed in a similar manner. All films heat treated at temperatures in excess of 570°C showed significant formation of a second $PbTi_3O_7$ phase. The films were characterized by electron microscopy and glancing-incidence angle X-ray diffraction.

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INTRODUCTION

The sol-gel process of hydrolysis and condensation of metal alkoxides to form polymeric ceramic precursors has been the subject of considerable research interest. While initial work demonstrated the relative ease in which various silica-based glass thin films could be fabricated, recent work has developed the potential of sol-gel processing methods for the deposition of polycrystalline electronic ceramic thin films. Processing techniques for sol-gel derived thin films of $BaTiO_3$,[1] $PbTiO_3$,[2] $Pb(Zr, Ti)O_3$,[3] PLZT,[4] and others have all been reported. With the exception of the work of Partlow and Greggi,[5] where observation of homoepitaxial growth of $LiNbO_3$ thin films was reported, there has been little information published relating to the potential of fabricating highly oriented and epitaxial thin films by sol-gel processing methods. While orientation of microstructure to enhance electrical characteristics is, in general, not a major issue in the development of ceramic dielectrics, there are specific exceptions where system performance is improved by film orientation. The electrical poling of ferroelectric ceramics to produce piezoelectric transducer and pyroelectric detector components is a case in point. Relative to thin film devices, there is, then, the need to develop economical processes for the fabrication of highly oriented ferroelectrics. In this work, the sol-gel method was investigated as a potential technique for the deposition of oriented and epitaxial $PbTiO_3$ thin films.

$PbTiO_3$ is a perovskite-type ferroelectric with a Curie temperature of 490°C and a large tetragonality (c/a = 1.06). In addition, the material possesses a relatively large spontaneous polarization P_s (75 $\mu C/cm^2$) and a small relative dielectric constant ε_r (350).[6,7] The synthesis of large, perfect $PbTiO_3$ single crystals is extremely difficult due to the volatility of lead at processing temperatures and the large contraction associated with the cubic-to-tetragonal transformation. Likewise, the utilization of bulk $PbTiO_3$ ceramics in various device designs has been precluded by the requirement for high operating voltage or small component area. Thin-film systems have been promoted as an effective means to circumvent these problems as a large electric field can be applied to the film over a relatively large area. In addition, the film can be integrated into a peripheral circuit via deposition onto a Si-based device directly. Okuyama and Hamakawa[8] reported on the rf-sputtering deposition of polycrystalline $PbTiO_3$ thin films on Si and mica. Matsubara, et al.[9] reported on the deposition of c-axis oriented $PbTiO_3$ films on $MgAl_2O_4$/Si for the fabrication of Si-monolithic devices. Recently, Iijima et al.[10] reported the rf-magnetron sputtering fabrication of a c-axis oriented $PbTiO_3$ thin film on (100) single crystal MgO and (100) Pt which possessed a small ε_r (~100) and a large pyroelectric coefficient (x 10^{-8} C/cm^2-K). As such, a c-axis oriented $PbTiO_3$ thin film would provide a suitable material for the development of pyroelectric infrared detector and piezoelectric transducer components.

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The sol-gel processing of $PbTiO_3$ has been the subject of extensive research study over the past few years, and the reader is referred to the reports of Budd, et al.[4] and Gurkovitch and Blum[11-13] for processing details. In addition, the recent report of Dekleva, et al.[14] is noted as the chemistry relating to the preparation of Pb-Ti complex alkoxides is reviewed. All previously reported sol-gel derived $PbTiO_3$ thin films possessed a randomly oriented, polycrystalline microstructure. The objective of the work conducted during this study was to investigate the potential of fabricating $PbTiO_3$ thin films with preferred orientation by a sol-gel processing method.

EXPERIMENTAL

Precursor Solution Preparation

Stock solutions of complex Pb-Ti alkoxide were prepared by reacting lead acetate* with titanium isopropoxide* in 2-methoxyethanol,* in a method similar to that reported by Gurkovitch and Blum.[11] The resulting yellow-gold solution had an equivalent $PbTiO_3$ concentration of approximately 66 wt%. The alkoxide solutions were handled as moisture-sensitive reagents and, as such, were stable.

Coating solutions were prepared at room temperature by first diluting the stock Pb-Ti alkoxide in 2-methoxyethanol to an equivalent $PbTiO_3$ concentration in the range of 5 to 15 wt%. The diluted solutions were acidified with concentrated HNO_3 to a resulting concentration of 0.1 M. Finally, hydrolysis was initiated by the addition of an aqueous 2-methoxyethanol solution. The total hydrolysis water charge was varied within the range of 1 to 6 mol H_2O per mol Ti (or Pb); i.e., approximately 1/2 to 3 times the stoichiometric water required for complete hydrolysis and condensation. Coating solutions were utilized immediately after synthesis, as next day precipitation was observed with high water concentration samples.

Coating Application and Processing

$PbTiO_3$ coatings were deposited on fused silica,† resistor-grade alumina,‡ and (100) cleaved single crystal MgO** substrates. The MgO substrates were selected due to the similarities in lattice parameter, oxygen packing symmetry, and thermal expansion properties as compared to $PbTiO_3$. Prior to use, the MgO substrates were degreased in an acetone ultrasonic bath, followed by immersion in an aqueous 10 vol% HCl solution, and a final rinsing in high-resistivity H_2O. Subsequently, the substrates were oven dried, and final particulate removal, if needed, was done by drag wiping using a lint-free tissue. Fused silica and alumina substrates were cleaned by drag wiping only.

Application of the $PbTiO_3$ precursor solution was accomplished by spin coating utilizing a commercial photoresist spinner◇ operated at 2000 rpm. The wet films were

*Aldrich Chemical Company, Milwaukee, WI 53233
†Accument Engineering Corp., Hudson, MA 01749
‡Materials Research Corp., Orangeburg, NY 10962
**J. J. Scott, Inc., Niagara Falls, Ontario, CANADA
◇Headway Research, Inc., Garland, TX 75042

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allowed to air dry for approximately 30 minutes, after which time they were transferred to an air atmosphere furnace for pyrolysis. The annealing time-temperature phase field for the crystallization of sol-gel derived $PbTiO_3$ reported by Gurkovitch and Blum[12] was utilized in determining heat-treatment parameters, with the exception that a heating rate of approximately 3°C per minute was used. A typical fully crystallized, single-layered film had a thickness of approximately 100 nm. Thicker films up to a nominal 500 nm were fabricated by multilayer coating techniques. In order to minimize film solubility, intermediate layers were heat treated for 30 minutes at 300°C. Annealing temperatures in the range of 450°C to 600°C were specifically investigated.

Microstructural Characterization

Microstructural characterization of the films was accomplished by X-ray diffraction (XRD) and scanning electron microscopy (SEM).* In addition, overall film quality was assessed by optical microscopy examination. An XRD system† equipped with a set of angular divergence soller slits in front of the detector element for parallel beam geometry operation was utilized throughout the study. A glancing-incidence X-ray diffraction technique was utilized to illuminate the structural details parallel to the substrate interface. Preferred orientation of films was inferred by a comparison of resulting XRD patterns to a $PbTiO_3$ powder pattern.

RESULTS

XRD Analysis

The resulting crystal structure of sol-gel derived $PbTiO_3$ thin films is sensitive to the annealing temperature. Thin films deposited on either fused silica or resistor-grade alumina exhibited a pyrochlore-type structure when annealed at temperatures less than 500°C for 4 hours. Similar to the results of Iijima et al.,[10] films annealed at temperatures in excess of 570°C showed significant formation of a $PbTi_3O_7$ phase. It was postulated that this observation was consistent with the loss of lead due to its significant vapor pressure at the processing conditions. Perovskite-type thin films were fabricated on alumina substrates which were annealed at a temperature of 550°C for 10 hours. Based on a comparison of XRD patterns to that of a sol-gel derived $PbTiO_3$ powder sample, films deposited on alumina were randomly oriented and polycrystalline.

In order to investigate the potential of epitaxial growth from sol-gel precursor solutions, thin films were deposited on (100) single crystal MgO substrates. MgO possesses the NaCl-type crystal structure with a lattice parameter of 4.21 Å. In comparison, the high temperature cubic form of $PbTiO_3$ has a lattice parameter of 3.98 Å, while the room temperature tetragonal form has lattice parameters a = 3.92 Å and c = 4.15 Å. Figure 1 shows XRD patterns for (a) a sol-gel derived $PbTiO_3$ powder, (b) a 500-nm-thick $PbTiO_3$ film on MgO annealed at 500°C for 4 hours, (c) a 200-nm-thick $PbTiO_3$ film on MgO annealed at 500°C for 4 hours, and (d) a 100-nm-thick $PbTiO_3$ film on MgO annealed at 500°C for 4 hours. The coating solution utilized for film deposition in this series had a molar H_2O to Ti ratio of 1. Figure 1a is a typical room temperature pattern for a polycrystalline perovskite which clearly illustrates the tetragonal crystal structure. While the pattern in Figure 1b still clearly indicates a polycrystalline film, there is observed significant orientation along both the (001) and {100} planes.

*JEOL Model JXA840 Electron Probe X-ray Microanalyzer
†Nicolet Model I2V/2000 Diffractometer

This result is similar to that reported by Iijima, et al.,[9] for the case of high rate sputtering. Figures 1c and 1d show the XRD pattern for films which are highly oriented along the {100} planes, which are the preferred orientation planes based on a lattice match criteria. It is noted that the degree of orientation for the 100-nm- and 200-nm-thick films is significantly enhanced as compared to the 500-nm film. At this time, it has not been established whether simple film thickness or the layered texture of the fabricated films is the primary factor in determining overall film quality.

In a recent report on the formation of oxide-thin films via sol-gel processing methods, Brinker, et al.[15] reviewed the relationship that precursor structure had to that of the corresponding thin films. For the polysilicate systems studied, it was shown that the degree of branching of the polysilicate precursor had a direct effect on the resulting morphology of the deposited film. Weakly branched precursor systems allowed for the interpenetration and rearrangement of polymer molecules during the film deposition process resulting in the formation of a thermodynamically favorable configuration of efficient packing and high density. In contrast, highly branched precursor systems lead to a high rate of irreversible entanglement of molecules during the deposition process which results in the formation of rigid structures. As such, rearrangement of precursor molecules is hindered and a nonhomogeneous, i.e., porous, film is formed. Based on these observations, it was anticipated that subsequent orientation of sol-gel derived crystalline films induced by a suitable single crystal substrate would be enhanced through the use of a low hydrolysis water, i.e., weakly branched, precursor solution. Moreover, it is known that for the case of deposition of sol-gel derived films on oxide substrates, there is the potential for condensation of the polymeric precursor to the surface hydroxyl species which may play a role in film epitaxy. Figure 2 shows the XRD pattern for two 100-nm-thick sol-gel derived $PbTiO_3$ films which were deposited on (100) MgO and annealed in air for 8 hours at 500°C. The top XRD pattern is for a film formed from a low water concentration, i.e., 2 gmol H_2O per gmol Ti, precursor solution, while the lower XRD pattern is for a film derived from a high water concentration; i.e., 6 gmol H_2O per gmol Ti, precursor solution. It is evident from the ratio of the intensities of the {100}, {110}, and (111) diffraction lines that film orientation along {100} planes is enhanced for the film prepared from the precursor solution with low hydrolysis water concentration.

Electron Microscopy Characterization

Figure 3 shows a low magnification and a high magnification SEM micrograph of a deposited film surface. The single-layer film was prepared from a coating solution with a molar H_2O to Ti ratio of 1.0 and had a thickness of approximately 100 nm. The deposited film was annealed in an air atmosphere at 500°C for 4 hours. The films exhibited a rough texture with an approximate grain size on the order of 0.2 μm. The observed film morphology is consistent with a fine-scale porosity. Sol-gel films which exhibit such porosity are not unusual, especially when the fraction of residual organic functionality of the precursor polymer is high.[5]

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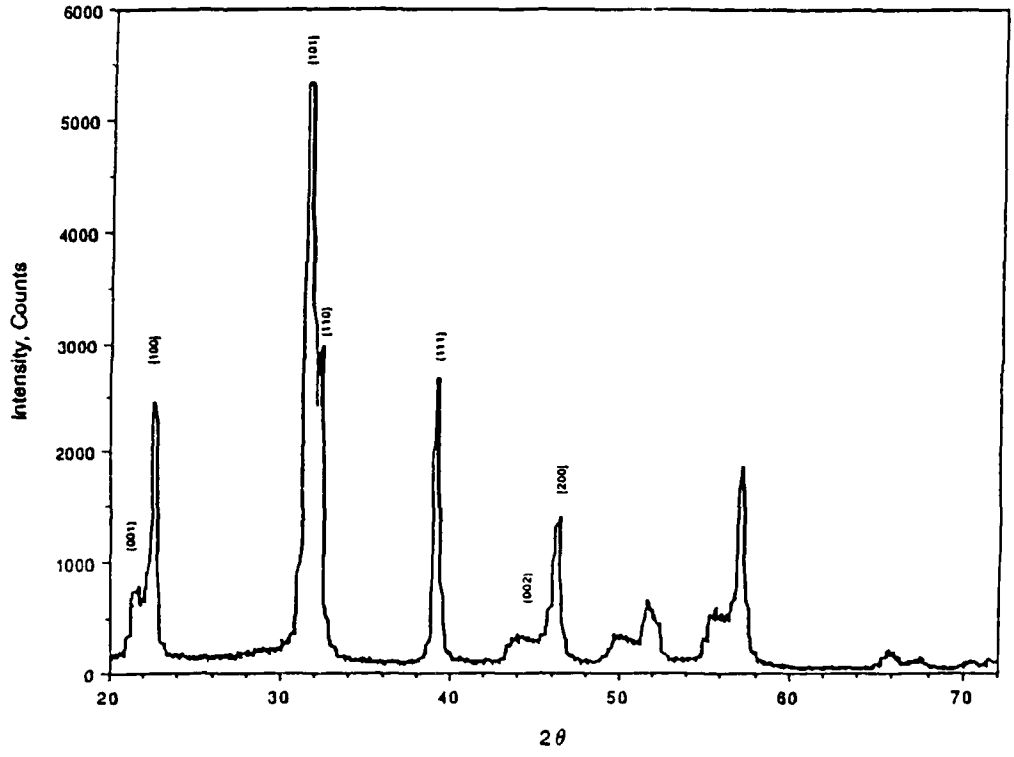
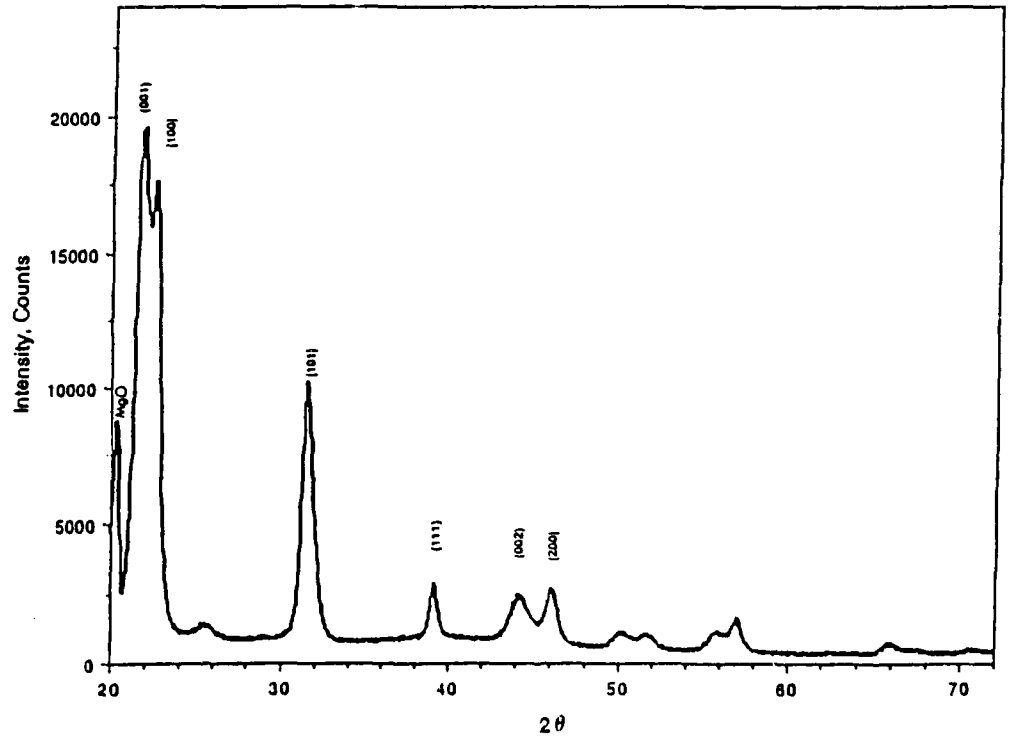
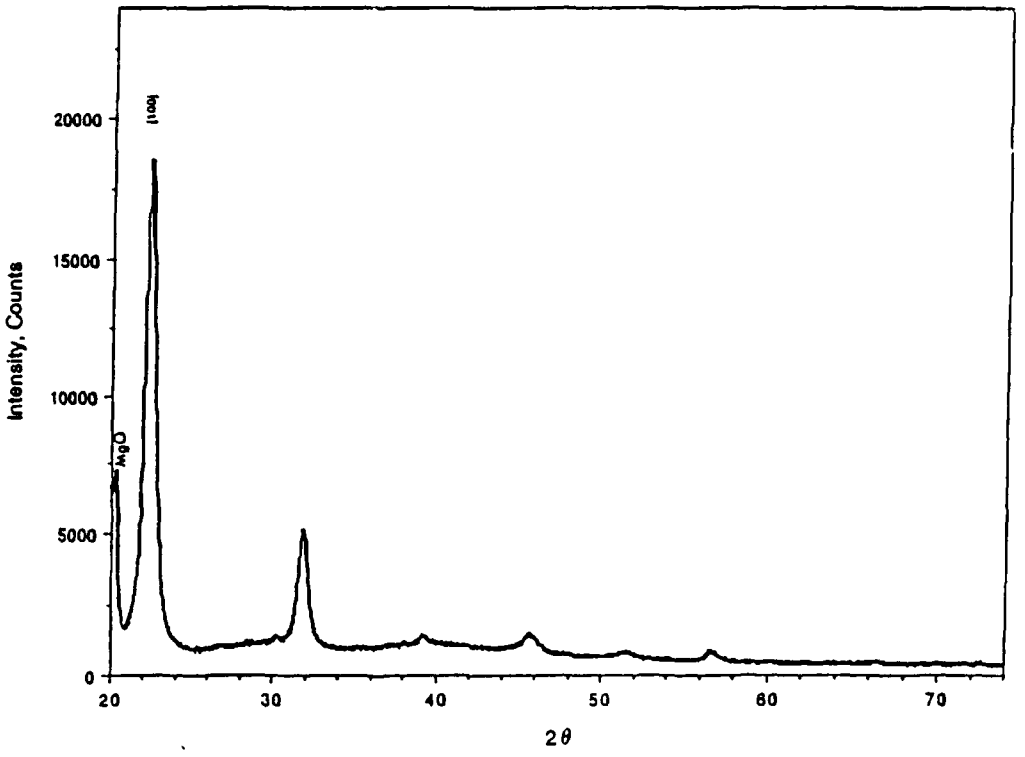


(a) Sol-Gel Derived $PbTiO_3$ Powder

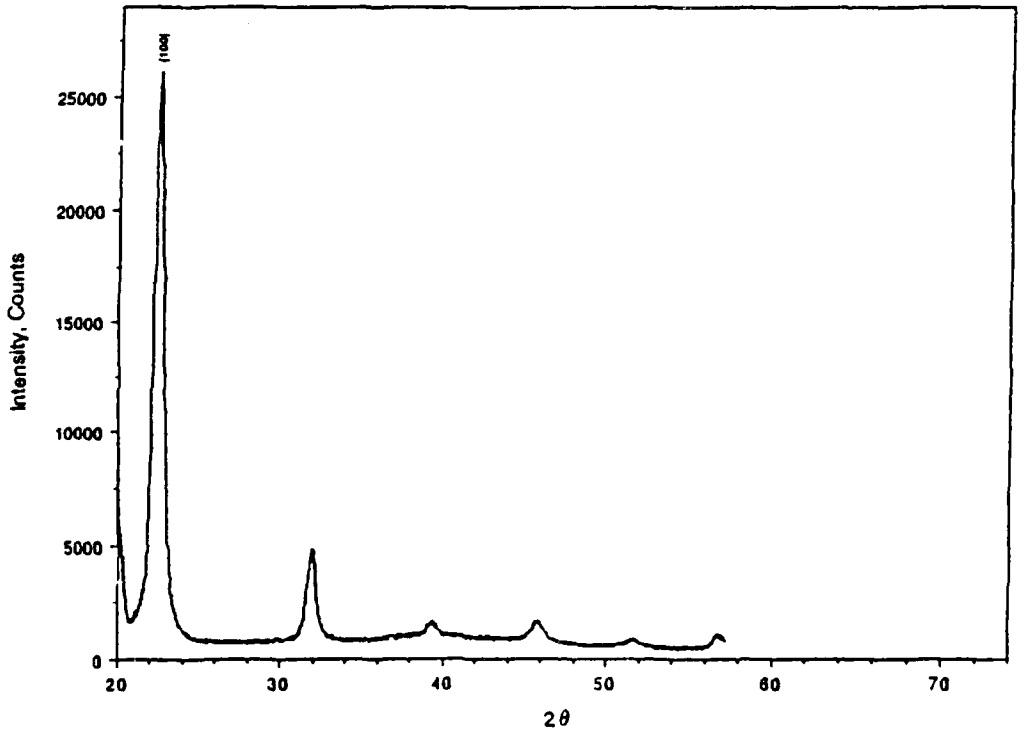


(b) A 500-nm-Thick $PbTiO_3$ Film on (100) MgO

Figure 1. X-ray diffraction patterns. Materials were annealed in air at 500°C for 4 hours.



(c) A 200-nm-Thick $PbTiO_3$ Film on (100) MgO



(d) A 100-nm-Thick $PbTiO_3$ Film on (100) MgO

Figure 1 (Cont'd). X-ray diffraction patterns. Materials were annealed in air at 500°C for 4 hours.

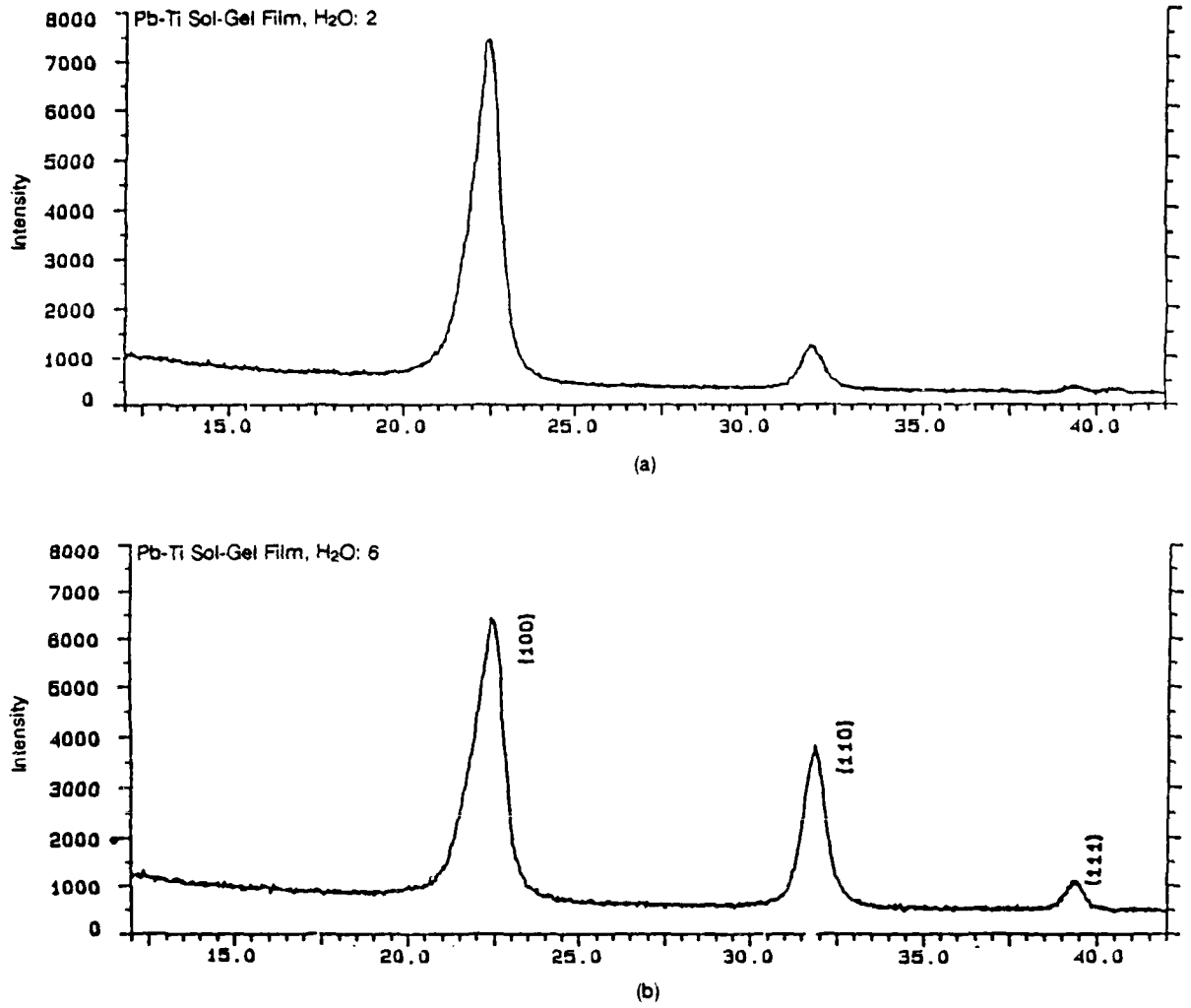


Figure 2. X-ray diffraction pattern for 100-nm-thick $PbTiO_3$ films deposited on (100) MgO prepared from precursor solutions of (a) low water concentration (2 gmol H_2O per gmol Ti) and (b) high water concentration (6 gmol H_2O per gmol Ti). The films were annealed in air at 500°C for 8 hours.

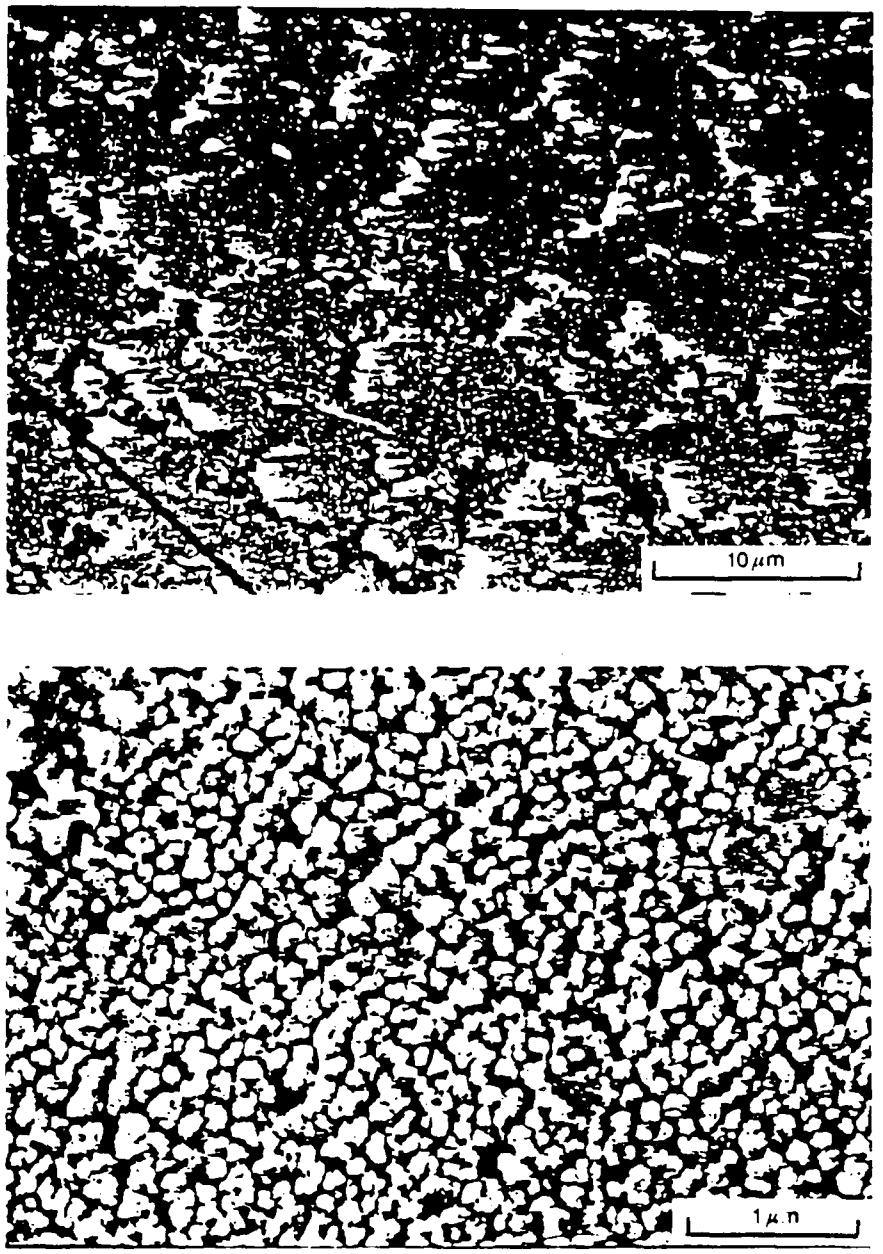


Figure 3. SEM micrographs of the top surface of a 100-nm-thick $PbTiO_3$ film which was annealed in air at 500°C for 4 hours.

CONCLUSIONS

The sol-gel processing of $PbTiO_3$ thin films by the crystallization of an amorphous ceramic precursor deposited on a number of substrates has been experimentally investigated. Film microstructure was influenced by the hydrolysis water concentration of the precursor solution, the thermal annealing history, and the substrate type. While films on fused silica and alumina annealed in air at temperatures less than 470°C showed a pyrochlore-type structure, films deposited on (100) MgO exhibited the perovskite structure. Additionally, all films heat treated to temperatures in excess of 570°C exhibited significant formation of a second $PbTi_3O_7$ phase associated with lead volatilization at the processing conditions. More interestingly, sol-gel-derived $PbTiO_3$ films deposited on (100) MgO were highly {100} oriented without poling treatment. This property may be of commercial significance in the development of array detector components, as it is difficult to uniformly pole a large group of small elements. Finally, it was noteworthy that crystalline films could be fabricated at temperatures less than the Curie point (490°C) and, as such, the large contraction associated with the cubic-to-tetragonal transformation was circumvented.

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U.S. Army Materials Technology Laboratory
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SYNTHESIS AND MICROSTRUCTURE OF HIGHLY ORIENTED $PbTiO_3$ THIN FILMS PREPARED BY A SOL-GEL METHOD -
Daniel F. Ryder Jr., Chiahong Chen, and William A. Spurgeon

Technical Report MTL TR 89-55, June 1989,
11 pp-illus.

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Key Words

Thin films
Lead titanate films
Sol-gel processing

Thin films of $PbTiO_3$ were deposited on fused silica, resistor-grade alumina, and single crystal (100) MgO by a sol-gel processing method. While the films deposited on silica and alumina substrates were randomly oriented and polycrystalline, highly {100} oriented $PbTiO_3$ films were grown on the MgO single crystals. The peroviskite-type structure was observed with films deposited on the single crystal MgO and annealed at temperatures as low as 470°C, while a pyrochlore-type structure was observed with films on fused silica and alumina processed in a similar manner. All films heat treated at temperatures in excess of 570°C showed significant formation of a second $PbTi_3O_7$ phase. The films were characterized by electron microscopy and glancing-incidence angle X-ray diffraction.

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